

Thermal Physics: entropy, temperature, free energy

※**Entropy**熵: logarithm of number of (stationary quantum) states of a system of particles.

量子定态

For a system in a stationary quantum state, all observable physical properties (energy) and number of particles are independent of time.

Each quantum state has a definite energy. States with identical energies belong to the same energy level.

※**Multiplicity/Degeneracy** of **an energy level**: number of quantum states with very nearly the same energy.

The energy of a system is the total energy of all particles(K+P+interactions between particles)

A quantum state of system is a state of all particles.

State of Particle: QM state of one element of system of particles (SHO n, spin ↑/↓)

Microstate of System: a single possible configuration of particle system.

Macrostate of System: gross parameters of, and constraints on system. ? ? ?

※**Orbital**: quantum states of a one-particle system.

$$\epsilon_s(N) = \frac{\hbar^2}{2M} \left(\frac{\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2)$$

energy of quantum state s of the N particle system $\epsilon_s(N)$:

Binary Model System: magnetic moment +m/-m >> magnet points up/down.

♥**Total model system magnetic moment/net system magnetization M**:

(N magnets each of magnetic moment m) $M = Nm - 2km = 2sm \in [-Nm, Nm]$

(possible values of M: N+1)

♥**Total number states of system**: 2^N .

Enumeration of States:

N: even, number of states

N_\uparrow : # of states with magnets up $N_\uparrow = \frac{1}{2}N + s$

N_\downarrow : # of states with magnets down $N_\downarrow = \frac{1}{2}N - s$

Spin Excess $2s = N_\uparrow - N_\downarrow$ $s \in [-\frac{1}{2}N, \frac{1}{2}N]$

net magnetic moment $M = 2sm$

All possible choice of system state:

$$(\uparrow + \downarrow)^N = \sum_{t=0}^N \frac{N!}{(N-t)!t!} \uparrow^{N-t} \downarrow^t = \sum_{s=-\frac{1}{2}N}^{\frac{1}{2}N} \frac{N!}{\left(\frac{1}{2}N+s\right)!\left(\frac{1}{2}N-s\right)!} \uparrow^{\left(\frac{1}{2}N+s\right)} \downarrow^{\left(\frac{1}{2}N-s\right)} \quad (\text{where } t = \frac{1}{2}N - s)$$

Multiplicity Function $g(N,s)$: number of states having the same value of s/fixed spin excess 2s.

$$g(N,s) = \frac{N!}{\left(\frac{1}{2}N+s\right)!\left(\frac{1}{2}N-s\right)!} = \frac{N!}{N_\uparrow!N_\downarrow!}$$

Sharpness: $g(N,s)$ is peaked sharply about $s=0$

$$\ln g(N,s) = \ln N! - \ln(\frac{1}{2}N+s)! - \ln(\frac{1}{2}N-s)!$$

[Stirling Approximation] $\ln N! = N \ln N - N$ $N! = \sqrt{2\pi N} N^N e^{-N}$ for $N \gg 1$

[Approximation] $\ln(1+x) = x - \frac{1}{2}x^2 + \dots$ for $x \ll 1$

$$g(N,s) \equiv g(N,0)e^{(-2s^2/N)} = \sqrt{\frac{2}{\pi N}} 2^N e^{(-2s^2/N)} \quad \text{for } s/N \ll 1 \text{ with } N \gg 1 \quad \text{Gaussian Approximation}$$

$g(N,s)$ center/maximum at $s=0$ $g_{\max}=g(N,0)$

$s^2 = \frac{1}{2}N$ value of $g = (1/e)g_{\max}$ fractional width of distribution

$N \uparrow$ distribution sharpened peak

Average Value of s^2

$$P(N,s) = g(N,s)/2^N \quad \langle f \rangle = \sum f(s)P(N,s) \quad f(s) = s^2 \quad \text{change } \sum \text{ to } \int (-\infty \text{ to } \infty)$$

$$\langle s^2 \rangle = \frac{\int_{-\infty}^{\infty} ds s^2 g(N,s)}{\int_{-\infty}^{\infty} ds g(N,s)} = \frac{1}{4}N$$

$$\langle s^2 \rangle = \frac{1}{4}N \quad \text{mean square spin excess} \quad \langle (2s)^2 \rangle = N$$

$$\text{root mean square spin excess} \quad \sqrt{\langle (2s)^2 \rangle} = \sqrt{N}$$

$$J = \frac{\sqrt{\langle (2s)^2 \rangle}}{N} = \frac{1}{\sqrt{N}}$$

Fractional Fluctuation of s^2 in $2s$

Energy of Binary Magnetic System:

$$\text{Potential Energy } U = -\vec{m} \cdot \vec{B}$$

$$U(s) = \sum_{i=1}^N U_i = -\vec{B} \cdot \sum_{i=1}^N \vec{m}_i = -2smB = -MB$$

$$\Delta \epsilon = U(s) - U(s-1) = 2mB$$

Multiplicity function for Harmonic Oscillators

Fundamental Assumption (of thermal phy): a closed system is equally likely/probable to be in any of the quantum states accessible to it.

Closed System: constant energy, number of particles, volume, relevant external parameters (which influence system, gEB)

Accessible (quantum state): properties compatible with system physical specification. (in range) state non-accessible: 0 probability $P(s)=0$

Accessible State of a System: a system microstate compatible with the state specification of energy, number of particles, etc.-- a microstate compatible with the system macrostate.

$$\delta U/U \ll 1 \quad \delta N/N \ll 1$$

Suppose a closed system with g equally likely accessible quantum states, s be a general state label $P(s) = 1/g$

$$\langle X \rangle = \sum_s X(s)P(s) = \sum_s X(s)1/g \quad (s: \text{accessible state})$$

Ensemble Average: average value of X
(property average over ensemble system)

Ensemble of Systems: group of systems constructed alike.

Thermal Contact: freely energy transfer between 2 system

Most Probable Configuration: system S_1, S_2 combine $S=S_1+S_2$ energy $U=U_1+U_2$

number of particle $N=N_1+N_2$ spin excess $s=s_1+s_2$ P34????

energy of combined system $U(s)=U(s_1)+U(s_2)=-2mBs$ constant so $s=s_1+s_2$ constant

multiplicity function of combines system: (number of accessible states of combine system)

$$g(N, s) = \sum_{s_1, s_2} g_1(N_1, s_1) g_2(N_2, s_2) = \sum_{s_1} g_1(N_1, s_1) g_2(N_2, s - s_1)$$

$$s_1 \in [-\frac{1}{2}N_1, \frac{1}{2}N_1] \quad N_1 < N_2$$

Configuration: set of all states with specified values of s_1 and s_2 .

Different configuration of combines system are characterized by different values of s_1

Most Probable Configuration: configuration for which $g_1 g_2$ maximum with $s_1 = s_1^{\text{hat/caret}}$.

Note: For system with large N, product $g_1 g_2$ is a very sharply peaked function of s_1 .

Thermal Equilibrium Values:

Average of a physical quantity over all accessible configurations \gg average over MPC

1. Two spin systems in the thermal contact:

$$\text{MPC: } \frac{s_1}{N_1} = \frac{s_2}{N_2} \quad \frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2}$$

2. **Thermal Equilibrium:**

The most probable division of total energy is the one for which the combined system has the maximum number of accessible states.

$$g(N, U) = \sum_{U_1} g_1(N_1, U_1) g_2(N_2, U - U_1)$$

Entropy: $\sigma(N, U) = \ln g(N, U)$ [dimensionless] g : # of accessible states of system

$$\left[\frac{\partial \sigma_1(N_1, U_1)}{\partial U_1} \right]_{N_1} = \left[\frac{\partial \sigma_2(N_2, U_2)}{\partial U_2} \right]_{N_2} \quad \text{in equilibrium}$$

$$\text{(Absolute) Temperature (in Kelvin): } \frac{1}{T} = k_B \left(\frac{\partial \sigma}{\partial U} \right)_N \quad \text{Boltzmann Constant } k_B = 1.381 \times 10^{-23} \text{ J/K}$$

$$\text{Fundamental Temperature: } \frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_N \quad [\text{J}] \quad \tau = k_B T \quad \text{Conventional Entropy: } S \text{ classic}$$

$$\text{definition } \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_N \quad S = k_B \sigma$$

$$\text{Total entropy change } \Delta \sigma = \left(\frac{\partial \sigma_1}{\partial U_1} \right)_{N_1} (-\Delta U) + \left(\frac{\partial \sigma_2}{\partial U_2} \right)_{N_2} (\Delta U) = \left(-\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \Delta U$$

$\tau_1 > \tau_2 \text{ so } \Delta \sigma > 0$

Thermal

Law of Increase of Entropy: $\sigma_{final} \approx \ln(g_1 g_2)_{max} \geq \sigma_{initial} = \ln(g_1 g_2)_{initial}$

total entropy always increases when 2 systems are brought into thermal contact.

entropy of a closed system tends to remain constant or increase when a constraint internal to system is removed.

Increase entropy: add particles, add energy, increase volume, decompose molecules, let a linear polymer curl up

The thermal equilibrium values of physical properties of a system are defined as averages over all states accessible when the system is in contact with a large system/reservoir.

If first system also large, thermal equilibrium properties 可以只考虑 MPC

Laws of Thermodynamics:

①Zeroth: $\tau_1 = \tau_2$ $\tau_2 = \tau_3$ then $\tau_1 = \tau_3$ $[\partial \ln(g_1)/\partial U_1]_{N_1} = [\partial \ln(g_2)/\partial U_2]_{N_2}$

If 2 systems are each in thermodynamic equilibrium with a third system, they must be in equilibrium with each other.

①First: heat is a form of energy. conservation of energy

②Second: increase of entropy

removing internal constraints in a closed system tends to cause the system entropy to remain constant or increase.

③Third: entropy of a system approaches a constant value as the temperature approaches (absolute) zero. (system goes to ground state)

Boltzmann Distribution:

one system S & reservoir R, $U_0 = U_R + U_S$ $U_R = U_0 - \epsilon_s$

$g_{R \times S} = g_{R \times 1} = g_R$

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g_R(U_0 - \epsilon_1)}{g_R(U_0 - \epsilon_2)} = \frac{e^{\sigma_R(U_0 - \epsilon_1)}}{e^{\sigma_R(U_0 - \epsilon_2)}} = e^{\Delta\sigma_R}$$

$$\sigma_R(U_0 - \epsilon) = \sigma_R(U_0) - \epsilon \left(\frac{\partial \sigma_R}{\partial U} \right)_{V,N} = \sigma_R(U_0) - \frac{\epsilon}{\tau}$$

where Taylor Expansion

$$\Delta\sigma_R = -\frac{\epsilon_1 - \epsilon_2}{\tau} \quad \text{so} \quad \frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{e^{-\frac{\epsilon_1}{\tau}}}{e^{-\frac{\epsilon_2}{\tau}}} = e^{\left(-\frac{\Delta\epsilon}{\tau}\right)}$$

Boltzmann Factor $e^{(-\Delta\epsilon/\tau)}$

Ratio of probability of finding system in a single quantum state 1 to state 2.

$$Z(\tau) = \sum_s e^{\left(-\frac{\epsilon_s}{\tau}\right)}$$

Partition Function:

sum over Boltzmann factor for all state s of system

$$P(\epsilon_s) = \frac{e^{\left(-\frac{\epsilon_s}{\tau}\right)}}{Z}$$

$$(\sum P(\epsilon_s) = 1)$$

(Thermal/Ensemble)

Average energy of system

$$U = \langle \epsilon \rangle = \sum \epsilon_s P(\epsilon_s) = \frac{\sum \epsilon_s e^{-\epsilon_s/\tau}}{Z} = \tau^2 \frac{\partial \ln Z}{\partial \tau}$$

Reversible Process: system remains infinitesimally close to the equilibrium state at all times during the process.

Pressure:

$$p = -\left(\frac{\partial U}{\partial V} \right)_\sigma = \tau \left(\frac{\partial \sigma}{\partial V} \right)_U$$

number of states σ in the ensemble is unchanged in reversible compression

Thermodynamic Identity: $\tau d\sigma = dU + p dV$ $dU = \tau d\sigma - p dV = T dS - p dV$

Thermal

TdS heat added to system, -pdV work done on system

Helmholtz Free Energy: $F = U - \tau\sigma = -\tau \ln Z$

differential of F: $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{\Psi}$ $p = -\left(\frac{\partial F}{\partial \Psi}\right)_{\tau} = -\left(\frac{\partial U}{\partial \Psi}\right)_{\tau} + \tau\left(\frac{\partial \sigma}{\partial \Psi}\right)_{\tau}$

For an ideal monatomic gas of N atoms of spin zero,

$$Z_N = (n_Q V)^N / N! ,$$

if $n = N/V \ll n_Q$. The quantum concentration $n_Q \equiv (M\tau/2\pi\hbar^2)^{3/2}$. Further,

Ideal Monatomic Gas: $pV = N\tau$; $\sigma = N[\log(n_Q/n) + \frac{5}{2}]$; $C_V = \frac{3}{2}N$.

Quantum-Mechanical Simple Harmonic Oscillators (QM-SHOs) frequency ω , state of oscillator specified by quantum number n :

Partition Function $Z = \sum_{s=0}^{\infty} e^{-s\frac{\hbar\omega}{\tau}} = \frac{1}{1 - e^{-\hbar\omega/\tau}}$

$$\langle s \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1}.$$

Planck Distribution Function:

Thermal average energy $\langle \varepsilon \rangle = \langle s \rangle \hbar\omega = \frac{\hbar\omega}{\exp(\hbar\omega/\tau) - 1}$ $U = \sum_n \langle \varepsilon_n \rangle = \sum_n \frac{\hbar\omega_n}{\exp(\hbar\omega_n/\tau) - 1}$

Stefan-Boltzmann law of radiation: $\frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3} \tau^4$,

Planck Radiation Law: $u_{\omega} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar\omega/\tau) - 1}$